Unit – One

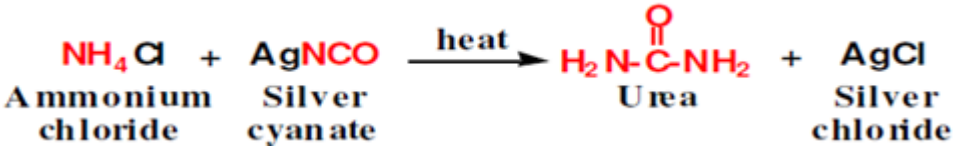
Bonding, Structure and Reactivity

Historical background of organic chemistry

Organic chemistry is the study of the compounds of carbon. Carbon is not the only element found in organic compounds. The elements found can be H, O, N, S, P and metals. All carbon containing compounds are not organic compounds. E.g. CO_2, CO, $NaCO_3$ they are inorganic b/c they are not sourced from living things.

Vitalism *"Organic"* -derived from living ***organism.*** Because of "Vital force", it was thought that organic compounds could not be synthesized in laboratory like inorganic compounds.

In 1828, Friedrich Wohler synthesized the first organic compound in his laboratory (urea).



Energy Levels and Atomic Orbitals

Energy level

Lowest-energy orbitals fill first: 1s → 2s → 2p → 3s →3p → 4s → 3d (**Aufbau ("build-up") principle**). The 1s orbital has the lowest energy. The 2s orbital is the next in energy and the 2p orbitals have the highest energies. The three 2p orbitals have the same energy, meaning that they are **degenerate**.

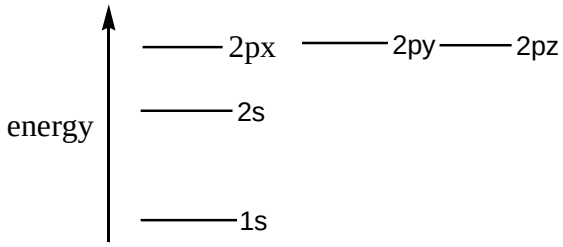
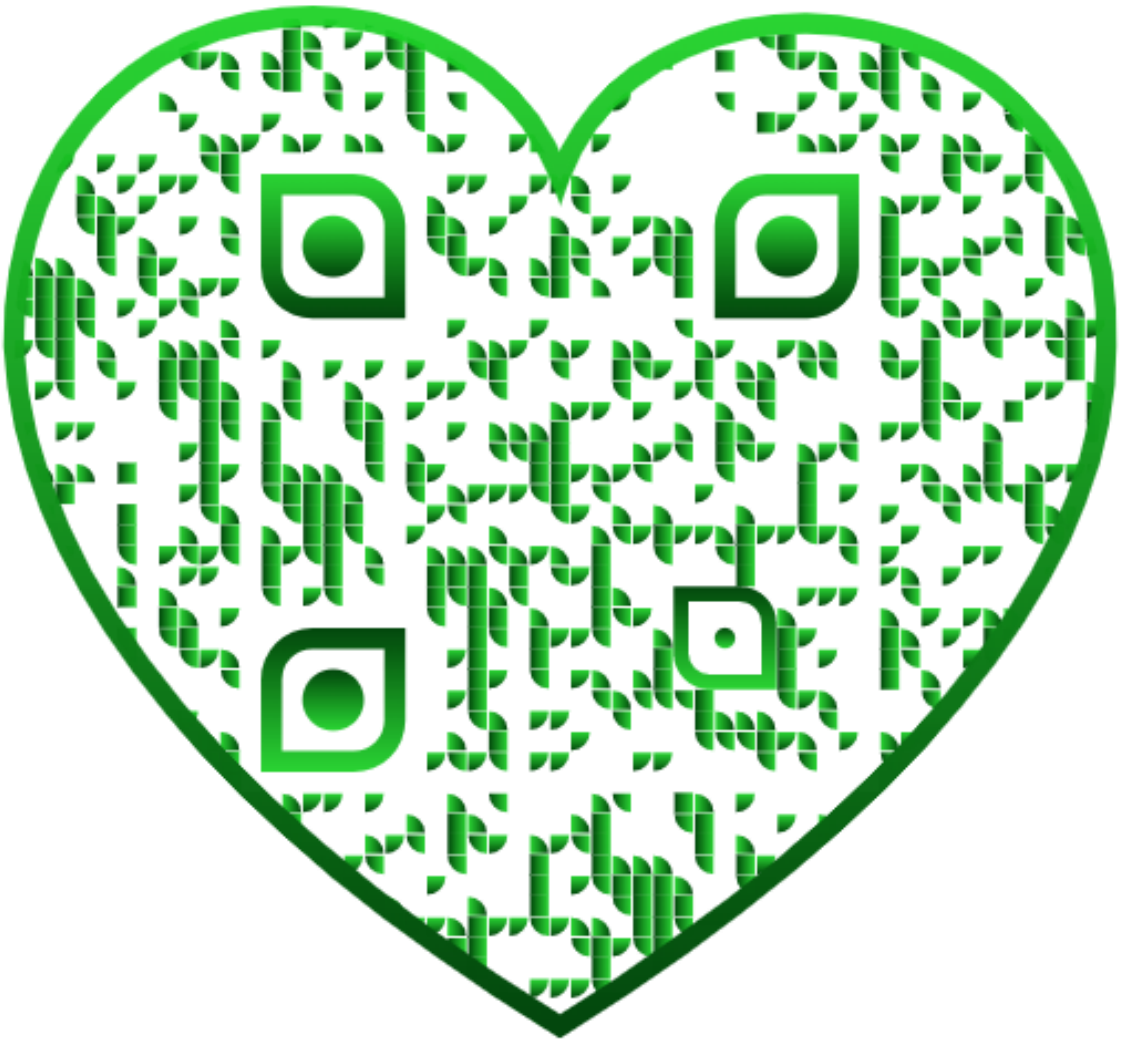


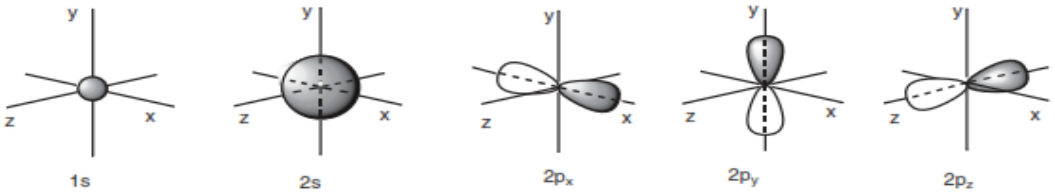
Fig.1.1. energy level and atomic orbitals

Atomic orbitals

Atomic orbitals are regions of space around the nucleus of an atom where an electron is likely to be found. AO corresponds to a region of space with high **probability** of finding an electron.

The atomic orbitals available for the six electrons of carbon are the **s** orbital in the first shell, the **s** orbital in the second shell and the three **p** orbitals in the second shell.





Only two electrons will be found in any orbital space as defined by thePauli Exclusion Principle. Thus the electronic configuration of carbon atom is $1s^2\ 2s^2 2p_x^1 2p_y^1$.The **Pauli Exclusion Principle** states that each orbital is allowed a **maximum of two electrons** and that these electrons must have **opposite <u>spins</u>**.

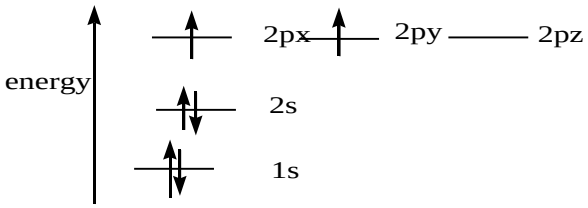


Fig.1.3. Electronic configuration of carbon

Bonding in Carbon Compounds

The property of carbon that makes it **unique is its ability to form bonds with itself** and **allows a large number of organic chemicals** with many diverse properties. Carbon has the property of forming **single**, **double** and **triple** bonds with itself and with other atoms.

This properties of carbon is known as **<u>catenation</u>**.

The types of bonds used by the carbon atom are known as **sigma (δ)** and **pi (π)** bonds.

Covalent bond forms when two atoms approach each other closely so that a singly occupied orbital on one atom overlaps a singly occupied orbital on the other atom. This can be describe by valance bond theory and molecular orbital theory.

1. Molecular Orbital Theory (MOT)

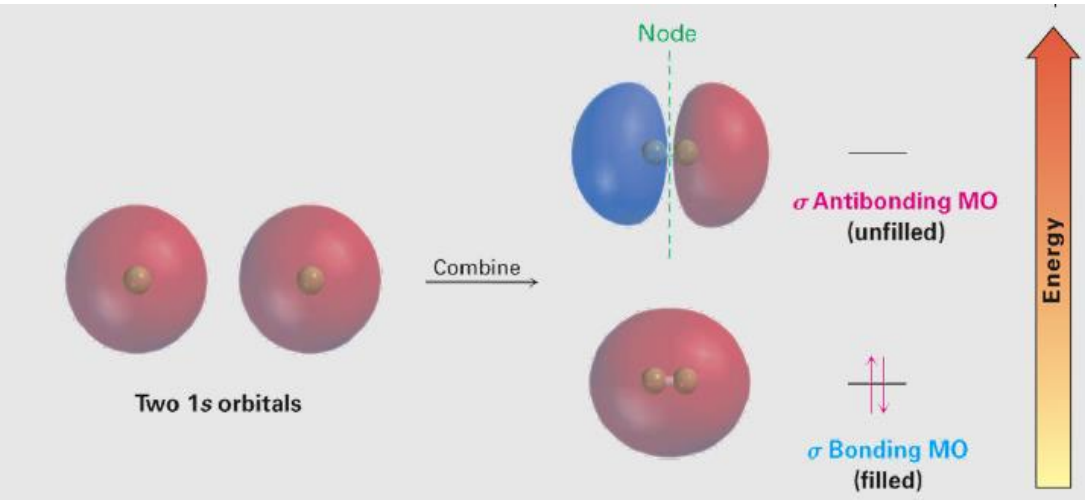
Atomic orbitals are capable of combining or overlapping, to produce new electron distributions called molecular orbitals (MOs). The description of covalent bond formation as resulting from a mathematical combination of atomic orbitals to form molecular orbitals. Valence electrons are in orbitals (called molecular orbitals) spread over entire molecule i.e. Valence electrons are delocalized.

MOs are derived from a linear combination (addition and subtraction) of atomic orbitals represented as wave functions of nearby atoms to form molecular orbitals. There are two possible combinations.

Additive combination (bonding) MO is lower in energy. Molecular orbital that is lower in energy than the atomic orbitals from which it is formed. Addition of AOs forms a bonding MO, which has a region of high electron density between the nuclei.

Subtractive combination (antibonding) MO is higher energy. Molecular orbital that is higher in energy than the atomic orbitals from which it is formed.S**ubtraction** of AOs forms an antibonding MO, which has a node, or region of zero electron density, between the nuclei.

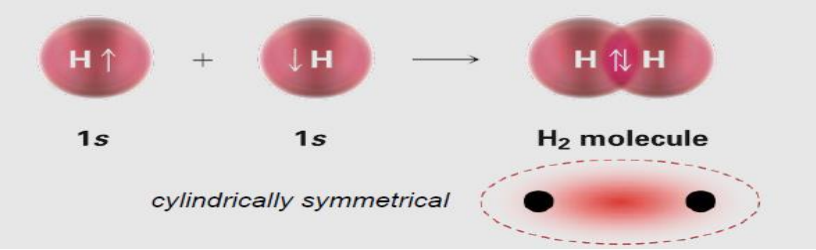
H_{1S}

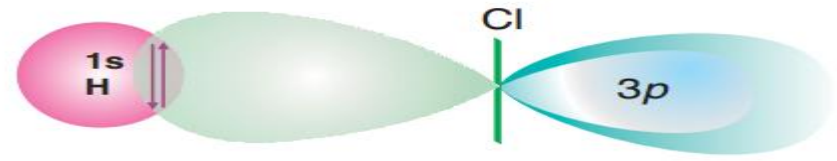


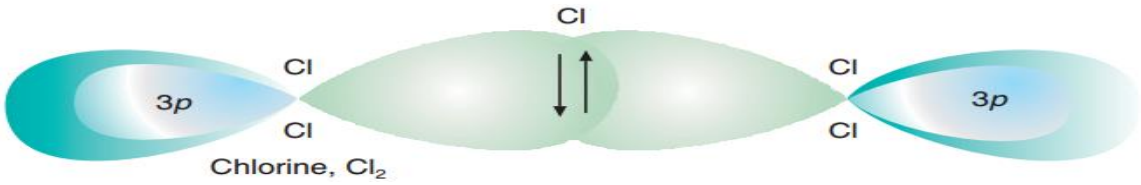
2. The valence bond theory (VBT)

The basic principle of valence bond theory is that a covalent bond forms when orbitals of two atoms overlap and the overlap region, which is between the nuclei, is occupied by a pair of electrons.

(i.e. high electron charge-density that results from the overlap of atomic orbitals between two atoms.)





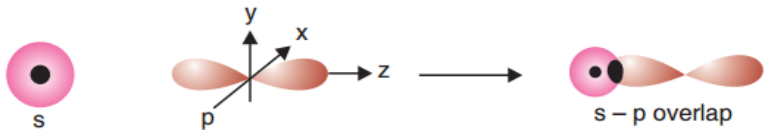


Overlap of Atomic Orbitals (Sigma and Pi Bonds)

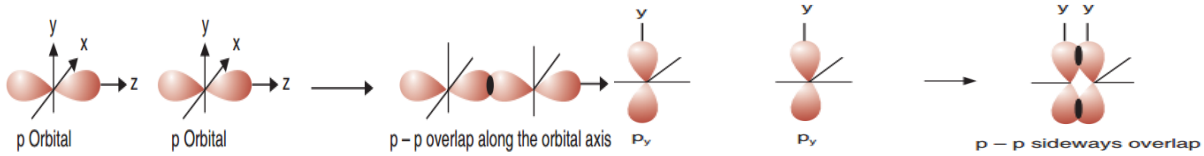
Various type of atomic orbital overlap leads to covalent bond formation. Three simple basic ones are *s-s* ,*s-p* and *p-p*.

1. *s-s* overlap in which half-filled *s* orbitals overlap

2. *s-p* overlap where half-filled *s* orbital of one atom overlaps with one of the *p* orbital having one electron only



3. *p-p*overlap in which two half-filled *p* orbitals overlap.



Note: *s* - *s* and *s* - *p* willalways overlap along the nuclear axis, which results only in **sigma bonds**.

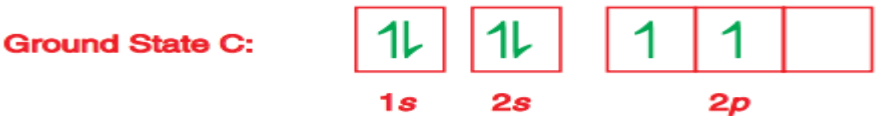
A side - to - side or parallel overlap forms another type of covalent bond called a **pi (π) bond**. It has two regions of electron density. One above and one below the sigmabond axis. One π-bond holds two electrons that occupy both regions of the bond.

Adouble-bond always consists of one σ and one π bond. The double-bond increaseselectron density between the nuclei. A triple bond consists of one σ and two π bonds.

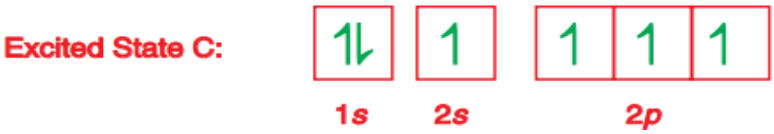
Orbital Hybridization

Valence bond theory employs the concept of hybridization. It is the overlap or blending of *s*, *p* and *d* orbitals to explain bond formation.

Example: The ground state electron configuration of carbon.



To excite the 2*s* electron to a higher energy sublevel, energy must be absorbed. The resulting electron configuration is that of an excited state having energy greater than the configuration in the ground state.



Valence bond theory proposes that the one 2*s* and all three 2*p* orbitals of the carbon atom 'mix' to produce four new orbitals that are equivalent to each other in energy and in shape. This blending is called hybridization and the resultant orbital as hybrid orbitals.

Hybridization provides a useful and convenient method of predicting the shapes of molecules.

In hybridization, *the number of new hybrid orbitals is equal to the total number of atomic orbitals that are combined.*

1. The 2s orbital is mixed with all three 2p orbitals. This is known as sp3 hybridization.
2. The 2s orbital is mixed with all two 2p orbitals. This is known as sp2 hybridization.
3. The 2s orbital is mixed with all one 2p orbitals. This is known as sp hybridization.

sp3 hybridization

Carbon, the central atom in a molecule of methane CH_4 has only two unpaired electrons in the ground state. The two electrons in the 2*p* level are not paired, *i.e.*, put into the same box, in accordance with Hund's rule. Carbon in its excited state can form four bonds. The one 2*s* and three 2*p*-orbitals of carbon are mixed to produce four new orbitals that are equivalent to each other in energy and in shape, but pointing in different directions.

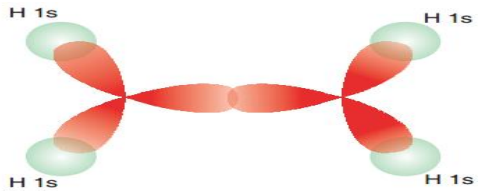
The four *sp*3 hybrid orbitals point to the corners of a regular tetrahedron, and make a bond angle of 109.50° in CH_4.

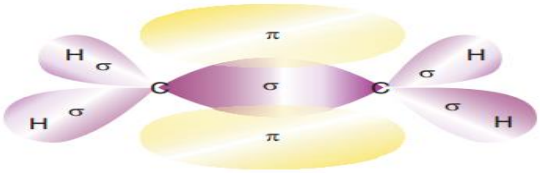
sp^{2}hybrid orbitals

In this case one s and two p orbitals mix together to form three sp^2 hybrid orbitals and are oriented in a trigonal planar geometry. The remaining p orbital if required form sideways overlapping with the other unhybridized p orbital of other C atom and leads to formation of $H_2C{=}CH_2$ bond as in H.

All the C–H bonds in C_2H_4 are formed by the overlap of *sp*2 hybrid orbitals of theC atoms with 1*s* orbitals of the H atom, with these orbitals directed along hypotheticallines joining the nuclei of the bonded atoms. A double covalent bond consists of oneσand one π bond.

This corresponds to H–C–H bond angles of 120°. To account for these bond angles in the valence bond method, you assume that the 2*s* and two of the 2*p* orbitals of the valence shell combine to produce *sp*2 hybridization of the two carbon atoms.





sp hybrid orbitals

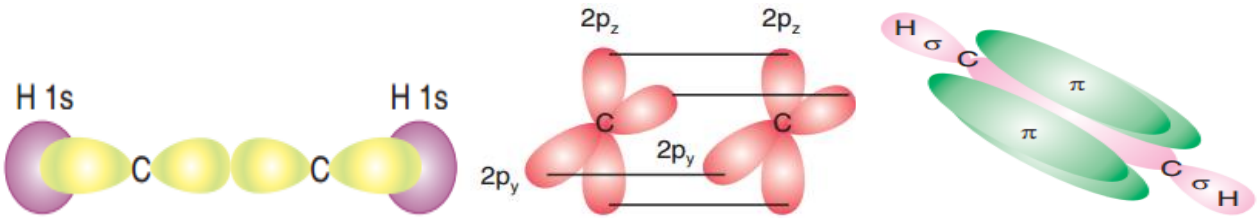
When two electron sets surround the central atom, you observe a linear molecular shape.

Consider the Ethyne (acetylene) molecule, C_2H_2. Its Lewis structure is:

$$H — C \equiv C — H$$

The molecule is linear, with 180° H–C–C bond angles. To account for these bond angles with thevalence bond method, we assume *sp* hybridization of the valence shell orbitals of thetwo C atoms.

In the C ≡ C bond in C_2H_2, as in all triple bonds, one bond is a σ-bond and twoare π- bonds.



CHAPTER TWO

Functional groups in organic chemistry

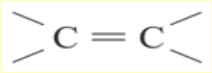
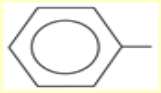
In organic chemistry, as the number of known organic compounds runs into millions, it is very difficult to study each and every compound individually. Thus, by grouping similar compounds together in a class or a family, it is easier to understand their properties, reactions etc. The structural features that allow classification of organic compounds into families are called **functional groups.**

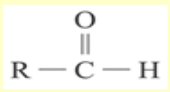
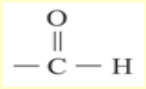
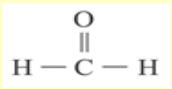
A functional group is an atom or group of atoms within a molecule that has a characteristic physical and chemical behavior.

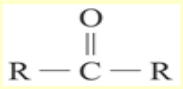
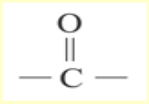
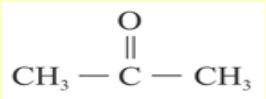
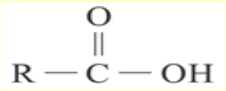
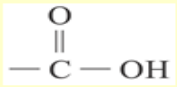
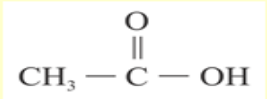
Functional groups are important in organic chemistry because:

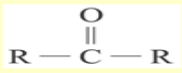
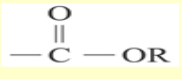
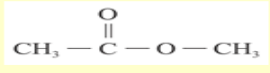
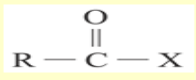
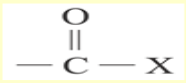
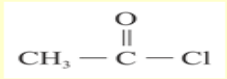
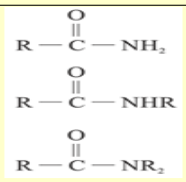
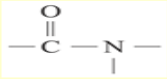
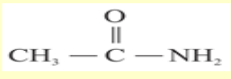
a. Predict the site of chemical reaction
b. Determine the physical properties of a molecule.
c. To classify organic compounds into families.
d. For naming organic compounds.

Classification of Organic Compounds

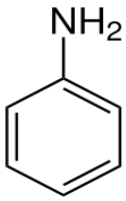
Family	General formula	Functional group	Example	
			Formula	IUPAC name
Alkane	RH	(Nil)	CH_3CH_3	Ethane
Alkene	$RCH = CH_2$ $RCH = CHR$ $R_2C = CHR$ $R_2C = CR_2$	 Carbon-carbon double bond	$CH_2 = CH_2$	Ethene
Alkyne	$RC \equiv CH$ $RC \equiv CR$	$-C \equiv C-$ Carbon-carbon triple bond	$HC \equiv CH$	Ethyne
Aromatic hydrocarbon	ArH	 Phenyl group		Benzene

Family	General formula	Functional group	Example	
			Formula	IUPAC name
Haloalkane	RX	— X halo group	CH_3Cl	Chloromethane
Alcohol	ROH	— OH hydroxyl group	CH_3OH	Methanol
Ether	R—O — R	— O — oxy group	$CH_3 — O — CH_3$	Methoxymethane
Aldehyde		 carbonyl group		Methanal

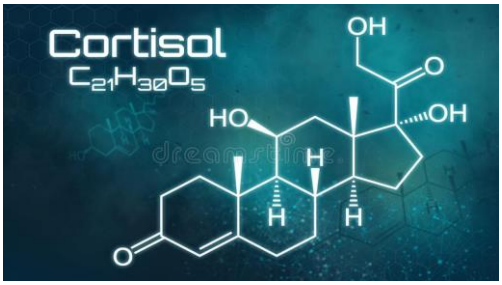
Family	General formula	Functional group	Example	
			Formula	IUPAC name
Ketone		 carbonyl group		Propanone
Carboxylic acid		 carboxyl group		Ethanoic acid
Amine	RNH_2 R_2NH R_3N	— N — | amino group	CH_3NH_2	Methylamine
Nitrile	RC≡N	— C ≡ N nitrile group	CH_3CN	Ethanenitrile

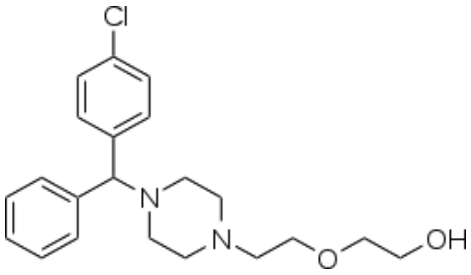
Family	General formula	Functional group	Example	
			Formula	IUPAC name
Ester		 ester group		Methyl ethanoate
Acyl halide		 acyl halide group		Ethanoyl chloride
Amide		 amide group		Ethanamide

Label all functional groups in the following molecules

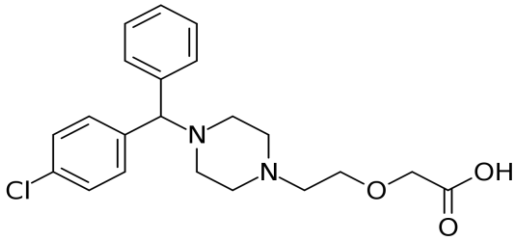


(Aniline)

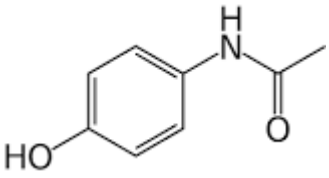




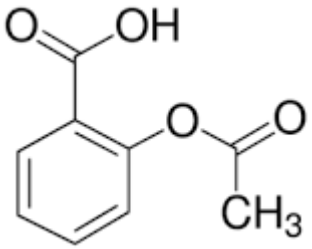
(Hydroxyzine)



(cetirizine)

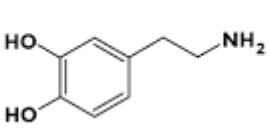


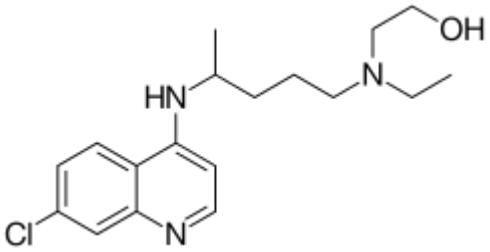
(pharacetamol)



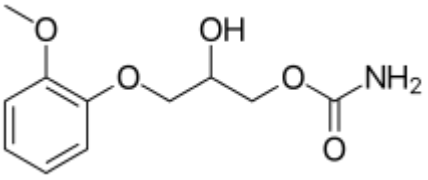
(Aspirin)

Loratadine is an antihistamine that reduces the effects of natural chemical histamine in the body. Histamine can produce symptoms of sneezing, itching, watery eyes, and runny nose.

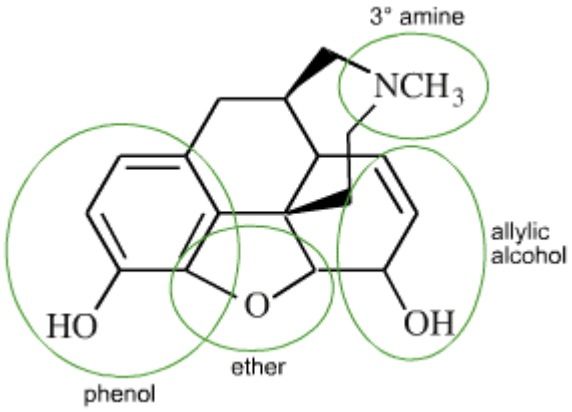




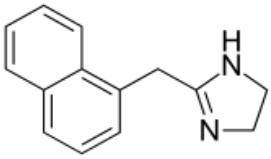
(Hydroxychloroquine)



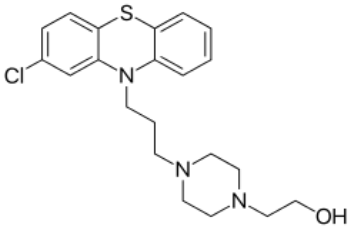
(Methocarbamol)



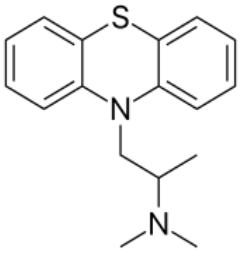
(morphine)



(Naphazoline)



(Perphenazine)



(Promethazine)

Classification of organic compounds

Hydrocarbons

Hydrocarbons are Compounds that contain only carbon and hydrogen. They can be classified in to saturated and unsaturated hydrocarbons based on the type of bonding between carbon atoms. Saturated hydrocarbons are those compounds of carbon and hydrogen containing only carbon-carbon single bonds. Alkanes (both straight and branched and cyclic alkanes) are examples of saturated hydrocarbons. Unsaturated hydrocarbons are compounds containing carbon-carbon multiple bonds either double or triple bonds. Alkenes are unsaturated hydrocarbons containing double bonds and alkynes, unsaturated hydrocarbons containing triple bonds.

Nomenclature of organic compounds

1. Alkanes

Are hydrocarbons that have the general formula $C_nH_{2n+2;}$ (where n = 1, 2, 3… etc). They are known as *saturated hydrocarbons* because all the bonds are single bonds (sigma bond) and have sp^3hybridization.

They occur in what is called a *homologous series* in which each successive compound differs from the next member of compound by a -CH_2 group. Members of a homologous series have similar chemical properties but the physical properties change gradually along the homologous series. For example the longer the carbon chain in the molecule (or the greater the molecular mass), The greater the attractive force between molecules, The higher the melting point, boiling point and density of the compound. Molecules with branched chains have lower boiling point and density than its straight-chain isomer. Why? Molecules with branched chains have melting point higher than its straight-chain isomer. Why?

Table 1: Some physical properties of the first 20 members of straight-chain alkanes

No	Molecular formula	Name of compound	State at rt& p	Melting point	Boiling point	Density in g/cm^3
1	CH_4	Methane	Gas	–183	–161	–
2	C_2H_6	Ethane	Gas	–172	–89	–
3	C_3H_8	Propane	Gas	–188	–42	–
4	C_4H_{10}	Buthane	Gas	–135	0	–
5	C_5H_{12}	Pentane	Gas	–130	36	0.626
6	C_6H_{14}	Hexane	Liquid	–95	69	0.657
7	C_7H_{16}	Heptane	Liquid	–91	98	0.684
8	C_8H_{18}	Octane	Liquid	–57	126	0.703
9	C_9H_{20}	Nonane	Liquid	–54	151	0.718
10	$C_{10}H_{22}$	Decane	Liquid	–30	174	0.730
11	$C_{11}H_{24}$	Undecane	Liquid	–26	196	0.740
12	$C_{12}H_{26}$	Dodecane	Liquid	–10	216	0.749
13	$C_{13}H_{28}$	Tridecane	Liquid	–7	233	0.753

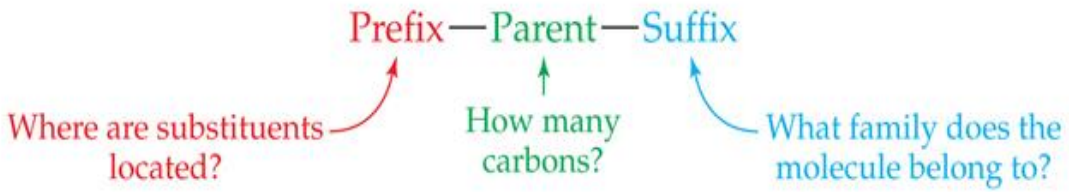
14	$C_{14}H_{30}$	Tetradecane	Liquid	–3	260	0.761
15	$C_{15}H_{32}$	Pentadecane	Liquid	10	271	0.769
16	$C_{16}H_{34}$	Hexadecane	Liquid	18	287	0.773
17	$C_{17}H_{36}$	Heptadecane	Liquid	22	302	0.778
18	$C_{18}H_{38}$	Octadecane	Solid	28	316	0.777
19	$C_{19}H_{40}$	Nonadecane	Solid	32	330	0.777
20	$C_{20}H_{42}$	Eicosane	Solid	37	344	0.785

Naming of alkanes

Nomenclature in organic chemistry is of two types: common (or ―trivial‖) and systematic. The Common system Works best for low molecular weight hydrocarbons that is for unbranched hydrocarbons. Beginning in 1892, chemists developed a set of rules for namingorganiccompounds based on their structures, which we now call the IUPAC rules, in whichIUPAC stands for the ―International Union of Pure and Applied Chemistry.‖ Use names tobranched alkanes most of the time.

Steps to give alkane a common name:

- Count the total number of carbon atoms in the molecule.
- Use the Latin root from the following slide that corresponds to the number of carbonatoms followed by the suffix ―**ane**.
- Unbranched hydrocarbons use the prefix *normal, or n-,*



Example

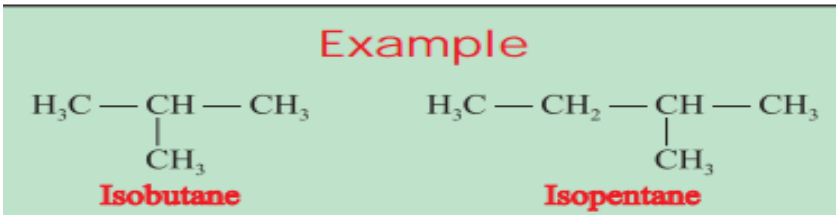
$H_3C — CH_2 — CH_2 — CH_2 — CH_3$

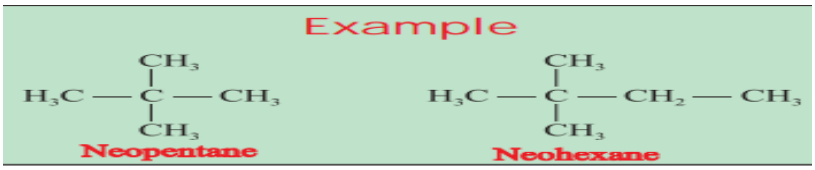
n-pentane

$H_3C — CH_2 — CH_2 — CH_2 — CH_2 — CH_3$

n-hexane

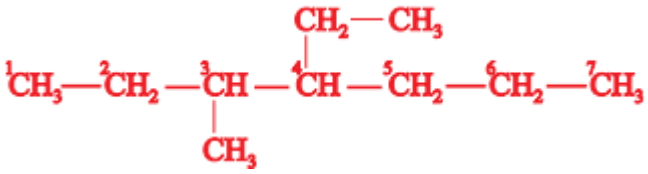
- Branched hydrocarbons use specific prefixes, **Neo-** and I**so-**. The prefixes **iso** is used whenthe side chain is placed next to the first carbon or before the last carbon while the prefixesneo is used when the central carbon is connected to four other carbon atoms.



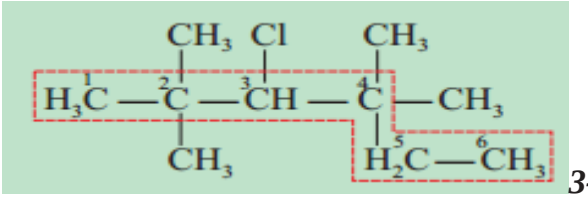


- The system of naming more branched and complex organic compounds are based on the IUPAC system and have the following rules or steps.
  - Find the longest continuous chain of carbon atoms as a parent structure.
  - Use a Latin root corresponding to the number of carbons in thelongest chain of carbons.
  - Follow the root with the suffix of ―ane‖ for alkanes
  - Carbon atoms not included in the chain are named as substituents preceding the rootname with Latin root followed by ―yl‖ suffix.
  - Number the carbons, starting closest to the first branch (start from the lowest possiblenumber).
  - Name the substituent's attached to the chain, using the carbonnumber as the locator inalphabetical order.
  - Use di-, tri-, etc., for multiples of same substituent.
  - Numbers are separated from each other by commas and from side chains by hyphens.
  - Mention the names of substituents before the parent name in alphabetical order.
  - If there are two possible chains with the same number of carbons, use the chain with themost substituents.

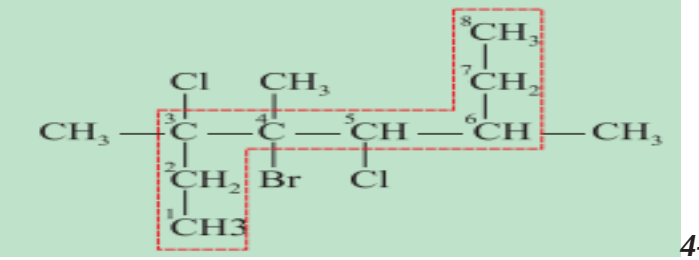
Example: give the IUPAC name of the following compounds.



4-ethyl-3- methylheptane



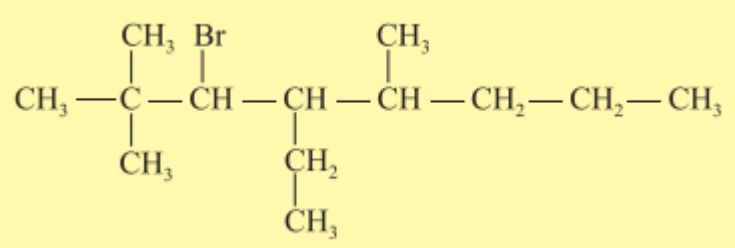
3-chloro-2,2,4,4- tetramethylhexane.



4-bromo-3,5-dichloro-3,4,6-trimethyloctane.

Activity

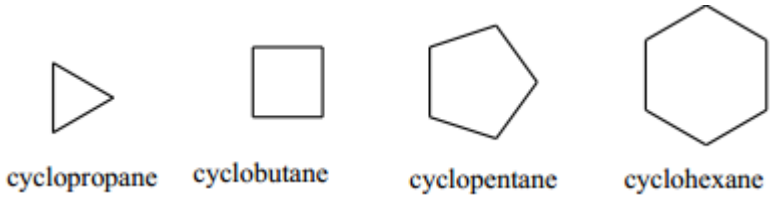
1. Give the IUPAC name of:



2. Write the structure of 2,2-dimethyl butane.
3. Write the structure of 2,3-dimethylpentane.

Cycloalkanes

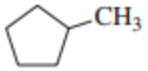
They are special class of alkanes that contain a ring of three or more carbons. They arefrequently encountered in organic chemistry and are characterized by the molecular formulaC_nH_{2n}. Some examples include:



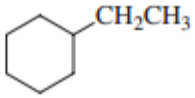
The rules for naming cycloalkanes resemble the rules for naming acyclic alkanes:

1. In the case of a cycloalkane with an attached alkyl substituent, the ring is the parent hydrocarbon unless the substituent has more carbon atoms than the ring. In that case, the substituent is the

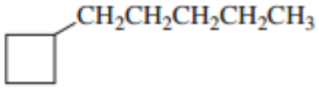
parent hydrocarbon and the ring is named as a substituent. There is no need to number the position of a single substituent on a ring.



methylcyclopentane

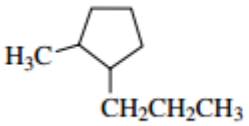


ethylcyclohexane

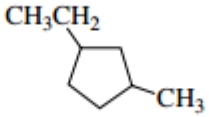


1-cyclobutylpentane

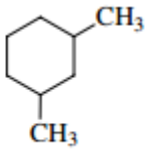
2. If the ring has two different substituents, they are cited in *alphabetical order* and the number 1 position is given to the substituent cited first.



1-methyl-2-propylcyclopentane

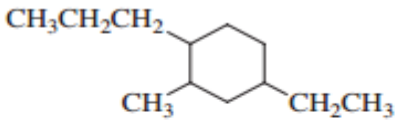


1-ethyl-3-methylcyclopentane

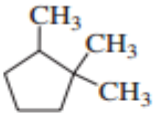


1,3-dimethylcyclohexane

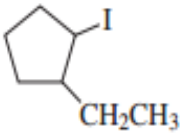
3. If there are more than two substituents on the ring, they are cited in alphabetical order. The substituent given the number 1 position is the one that results in a secondsubstituent getting as low a number as possible. If two substituents have the samelow number, the ring is numbered—either clockwise or counterclockwise inthe direction that gives the third substituent the lowest possible number.



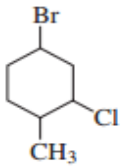
4-ethyl-2-methyl-1-propylcyclohexane
not
1-ethyl-3-methyl-4-propylcyclohexane
because 2 < 3
not
5-ethyl-1-methyl-2-propylcyclohexane
because 4 < 5



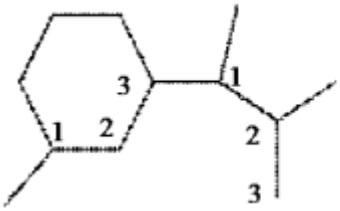
1,1,2-trimethylcyclopentane
not
1,2,2-trimethylcyclopentane
because 1 < 2
not
1,1,5-trimethylcyclopentane
because 2 < 5



1-ethyl-2-iodocyclopentane

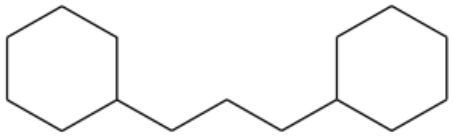


4-bromo-2-chloro-1-methylcyclohexane



1-methyl-3-(1,2-dimethylpropyl)cyclohexane

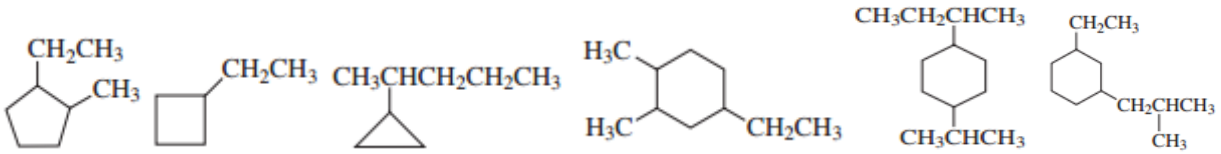
4. When more than one ring system is attached to a single chain then the compound is named as an alkane and the ring is named as a substituent.



1,3 -di cyclohexylpropane

Activity

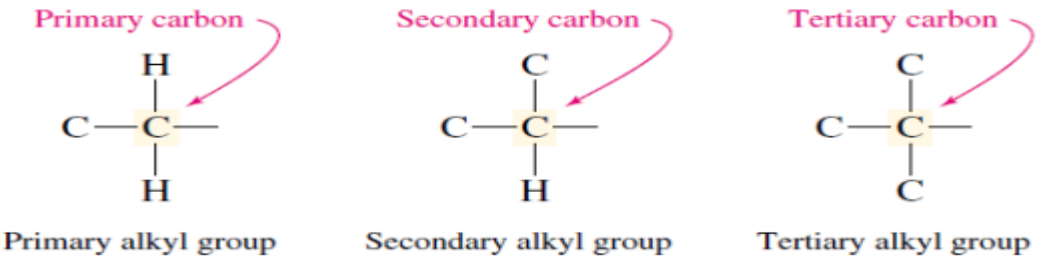
1. Give the systematic name for each of the following compounds:



2. Draw the structure of:
    a. Pentyl –cyclopentane
    b. 1, 1-diethyl-4-hexylcyclooctane.

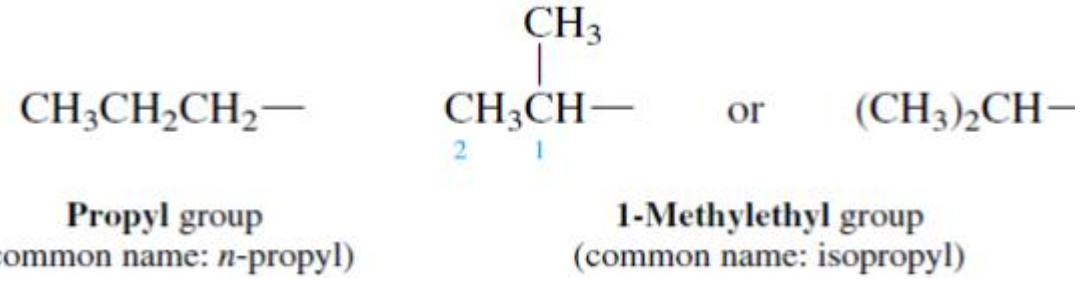
Alkyl groups

An alkyl group lacks one of the hydrogen substituents of an alkane. A methyl group (CH_3-) is an alkyl group derived from methane (CH_4). Unbranched alkyl groups in which the point of attachment is at the end of the chain are named in IUPAC nomenclature by replacing the suffix‘s -ane by -yl. For example CH_3CH_2-, $CH_3(CH_2)_5CH_2$- represent the name for ethyl and heptyl group respectively.



Ethyl (CH_3CH_2-) and heptyl [$CH_3(CH2)_5CH_2$-], are examples of primary alkyl groups.

Branched alkyl groups are named by using the longest continuous chain that begins at the point of attachment as the base name. Thus, the systematic names of the two C_3H_7alkyl groups are propyl and 1-methylethyl. Both are better known by their common names, n-propyl and isopropyl, respectively.



Formulas, names and structures of some alkyl groups.

Formula of alkane	Formula of alkyl radical	Condensed structure of alkyl radical	Common name of alkyl radical
CH_4	CH_3–	CH_3–	Methyl
C_2H_6	C_2H_5–	CH_3CH_2–	Ethyl
C_3H_8	C_3H_7–	$CH_3CH_2CH_2$– $CH_3—CH(CH_3)—$	*n*-Propyl Isopropyl
C_4H_{10}	C_4H_9–	$CH_3CH_2CH_2CH_2$– $CH_3CH(CH_3)—CH_2—$ $H_3C—CH_2—C(CH_3)(H)—$ $H_3C—C(CH_3)_2—$	*n*-Butyl Isobutyl sec-Butyl (s-Butyl) tert-Butyl (t-Butyl)

2. Alkenes

- Are unsaturated hydrocarbons that contain a carbon–carbon double bond
- They have the general formula CnHn, where n = 2, 3,4 etc
- A carbon– carbon double bond is both an important structural unit and an importantfunctional group in organic chemistry.

Alkene nomenclature

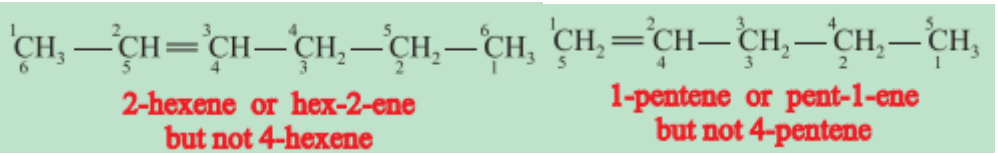
- We give alkenes IUPAC names by replacing the –*ane* ending of the corresponding alkanewith -*ene*.

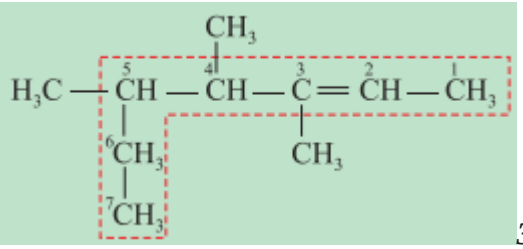
- The two simplest alkenes are **ethene**and **propene.** Both are also well known by theircommon names *ethylene* and *propylene.*

Common name: ethylene **Common name**: propylene

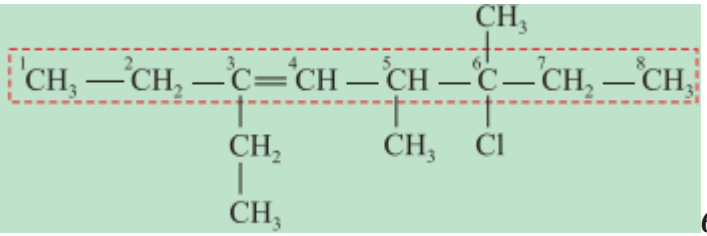
- The longest continuous chain that includes the double bond forms the base name of the alkene, and
- The chain is numbered in the direction that gives the doubly bonded carbons their lowernumbers. The locant (or numerical position) of only one of the doubly bonded carbons isspecified in the name; it is understood that the other doubly bonded carbon must followin sequence.

Example:

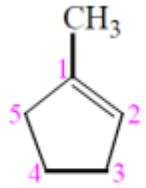




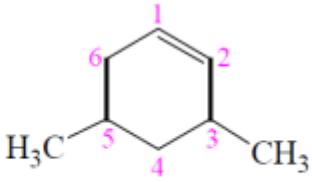
3, 4, 5-trimethyl-2-heptene or 3, 4, 5-trimethyl hept-2-ene



6-chloro-3-ethyl-5,6-dimethyl-3-octene

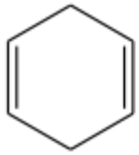


1-Methylcyclopentene
(*not* **2-methylcyclopentene**)

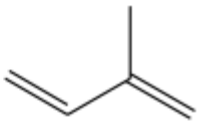


3,5-Dimethylcyclohexene
(*not* **4,6-dimethylcyclohexene**)

- If more than one double bond is present, indicate the position of each, and use the suffixes-diene, triene etc.

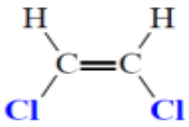


cyclohexa-1,4-diene

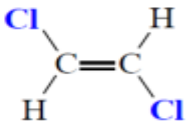


2-methyl-1,3-butadiene

***Cis*- and *trans*-alkenes:**



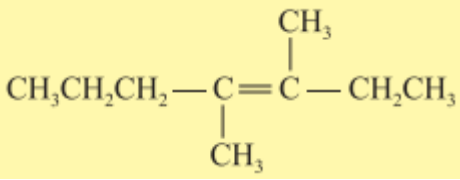
***cis*-1,2-Dichloroethene**

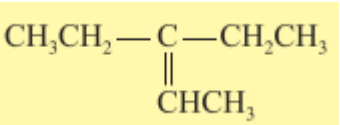


***trans*-1,2-Dichloroethene**

Activity

1. Give the IUPAC name for the following

a 

b 

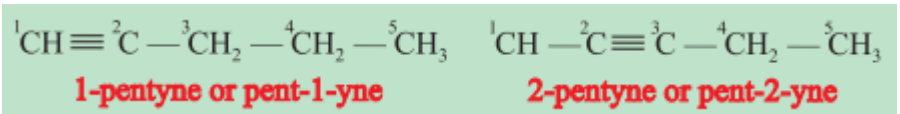
2. Write the structure of each of the following compounds:
   a. 3-methyl-3-heptene
   b. 3,4-diethyl-1-hexene

3. Alkynes

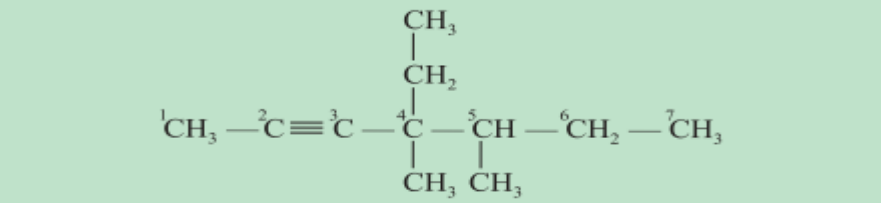
- Are unsaturated hydrocarbons that contain a carbon–carbon triple bond.
- They have the general formula CnH2n-2 , where n = 2, 3,4 etc

Nomenclature of alkyne

a. alkynes are named in much the same way as alkenes replacing –ene to -yne



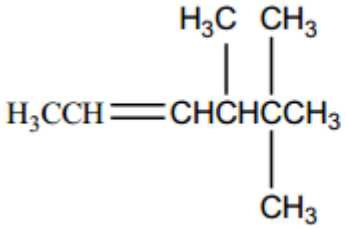
1-pentyne or pent-1-yne 2-pentyne or pent-2-yne

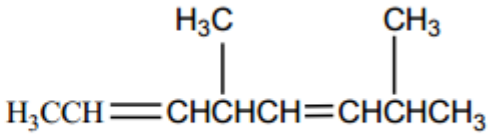


4-ethyl-4,5-dimethyl-2-heptyne or 4-ethyl-4,5-dimethyl-hept-2-yne

Activity

1. Give the IUPAC name of the following compounds.

a. 

b. 

2. Draw the structure corresponding to the following IUPAC names

a. 2-methyl-1.5-hexdiene

b. 3-ethyl-2, 2-dimethyl-3-heptene

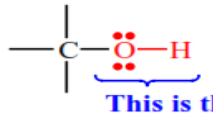
c. 4-tert-butyl-2-methyl- 2-heptyne

d. 2, 3, 3-trimethyl 1, 4, 6-octatriene

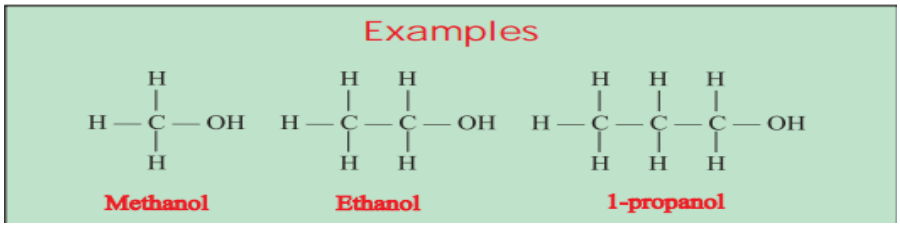
4. Alcohols

What do you think when you hear the word “alcohol”? Can you define alcohol? Give afew examples of the uses of alcohols. Most people think of two common alcohols- thesubstance that intoxicates people and the one used in clinics and hospitals. However, thereare many types of alcohol. The only alcohol present in all alcoholic beverages is called ethanol. Other alcohols are used for different purposes.

Alcohols are hydroxyl derivatives of hydrocarbons that can be obtained by replacing oneor more hydrogen atom(s) of a hydrocarbon with the hydroxyl (–OH) group. The hydroxylgroup is the functional group of alcohols.



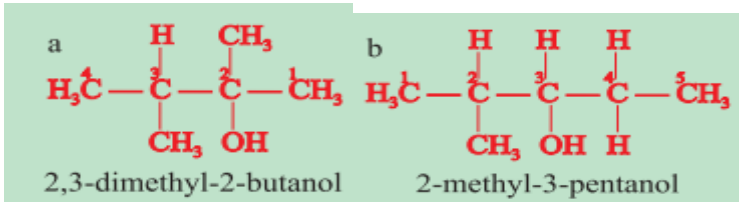
This is the functional group of an alcohol

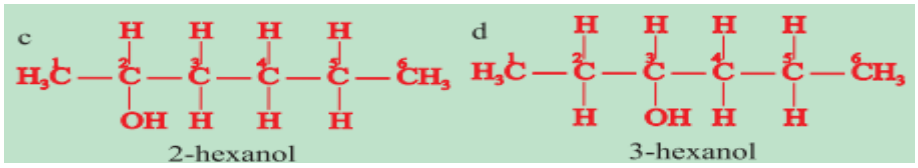


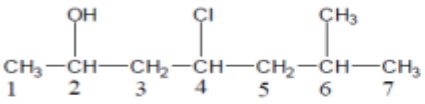
Nomenclature of Alcohols

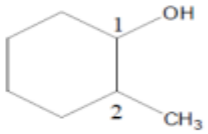
In the IUPAC system of nomenclature of alcohols containing side chains or –OH groups indifferent positions, the longest chain to which the –OH group is attached, is chosen as aparent structure. The chain is then numbered, starting from the end closer to the carbonatom to which the –OH group is bonded. The other rules are similar to the nomenclature ofhydrocarbons.

Example



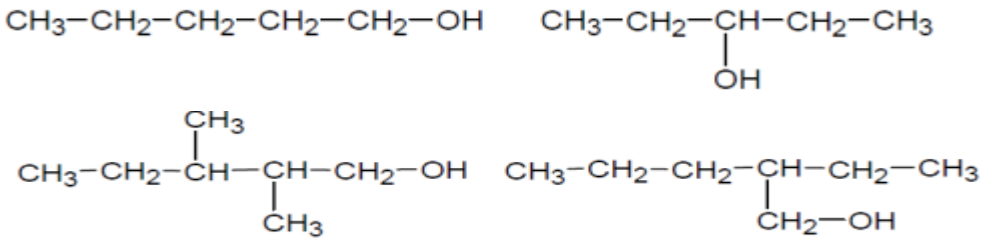


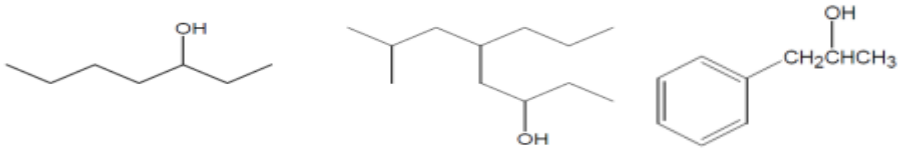

4-chloro-6-methyl-2-heptanol


2-methylcyclohexanol

Activity

1. Give IUPAC name for the following:





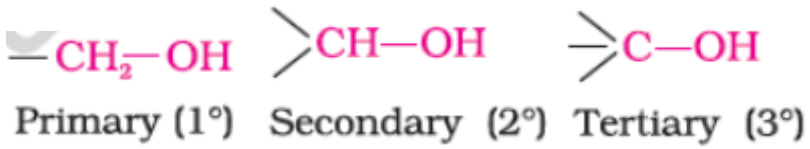
Classification of monohydric Alcohols

Monohydric alcohols can be classified as primary (1°), secondary (2°) and tertiary (3°)alcohols, depending on the number of hydrocarbon groups (*alkyl groups*) attached to the carbon atom to which the hydroxyl group is bonded.

Alcohols can also classified monohydric, dihydric and polyhydric alcohols according to how many hydroxyl groups are attached to carbon atom**.**

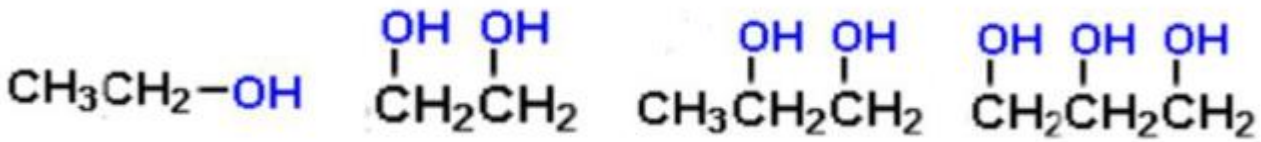
Monohydric alcohols

- Alcohols that possess only one hydroxyl group



Polyhydric alcohols—alcohols that possess more than one hydroxyl group.

• An alcohol in which two hydroxyl groups are present is named as a diol, one containing three hydroxyl group is named as a triol, and so on.



1-Ethanol (ethyl alcohol) **1, 2-Ethanediol (ethylene glycol)** **1, 2-Propanediol (propylene glycol)** **1,2,3-Propanetriol (glycerol)**

Activity

1. Draw structural formulas for the following molecules:

a. 3-ethylcyclopentanol

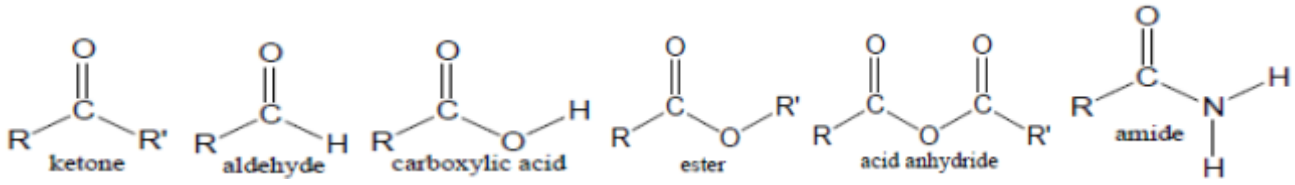
b. 3-ethylphenol

c. 3-methyl-2,4-pentanediol

2. Draw and name all of the possible isomers of hexanol ($C_6H_{14}O$)

5. Carbonyl group

The carbonyl group (C=O) is found in aldehyde, Ketones and many other functional groups. The carbon and oxygen in the carbonyl group are sp2 hybridization with bond angle of 120^0. The most common compound containing carbonyl groups are aldehydes and ketones. In ketone two carbon groups are attached to the carbonyl carbon while in aldehyde at least one hydrogen is bonded to the carbonyl carbon instead of the other carbon.

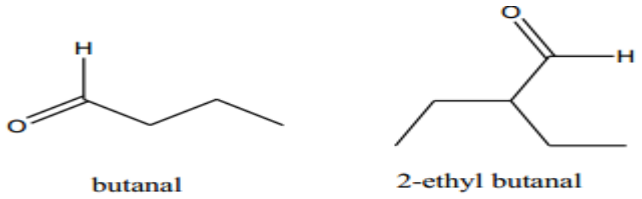


5.1. Nomenclature of aldehyde

- Select the longest chain containing the carbonyl carbon.
- Replace the –e ending of the parent alkane by the suffix –al
- The carbonyl carbon is always numbered 1.it is not necessary to include thenumber in the name.
- Name the substituents attached to the chain in the usual way.

Example

Name the following aldehydes.

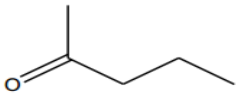


5.2. Nomenclature of ketones

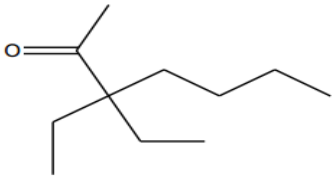
- Select the longest chain containing the carbonyl carbon.
- Replace the –e ending of the parent alkane by the suffix –one.
- Number the chain starting with the end closest to the ketone groups (the carbonyl carbon should have the lowest possible number).
- Name the substituents attached to the chain in the usual way.

Example

Name the following ketones



pentan-2-one



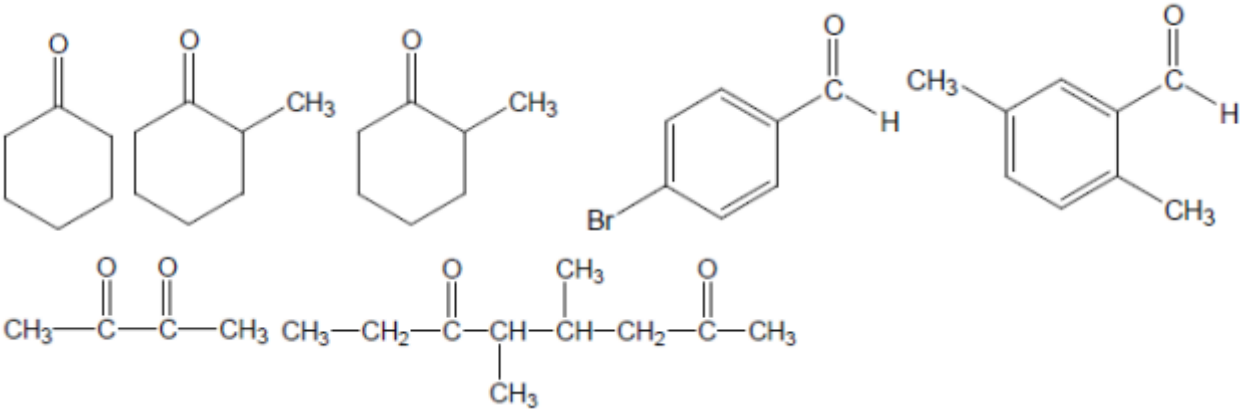
3,3-diethylheptan-2-one

Other Nomenclature Rules

- ✓ In cyclic ketones, the carbonyl group is always numbered —1‖; this does not need to be included in the name. The numbering continues clockwise or counterclockwise to give the lowest number for the next substituent.
- ✓ Molecules with more than one ketone group are named by preceding the suffix with acounting prefix (dione, trione, etc.); position numbers must be used for each ketonegroup.
- ✓ Aromatic aldehydes (containing an aldehyde group directly attached to a benzene ring)are named after the parent compound benzaldehyde. (The carbon to which the aldehyde group is attached is carbon 1).

Activity

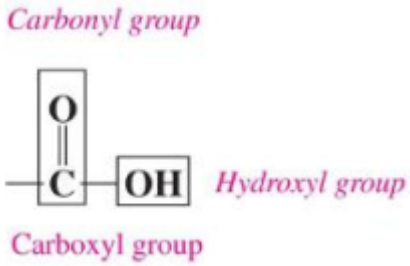
1. Name the following compounds:



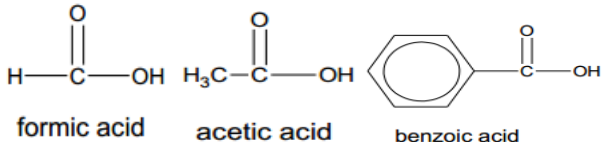
2. Draw the structure of the following compounds.
   a) 3-ethyl-2-pentanone
   b) 2,4,6-trimethyl heptanal
   c) 4-chloro-2-phenylpentanal
   d) Para-nitrobenzaldehyde

5.3. Carboxylic acids and their derivatives

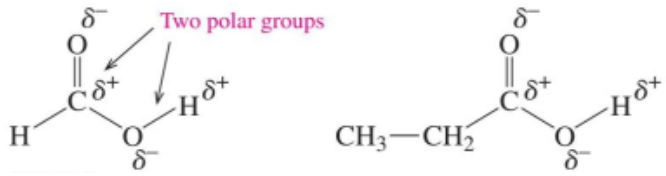
A **carboxyl group** is a carbonyl group (C = O) with a hydroxyl group (-OH) attached to the carbonyl carbon atom.



Carboxylic acids can be aliphatic acids which have an **alkyl group** bound to the carboxyl group and an aromatic acid that has an **aryl group** bound to the carboxyl group .Since carbon can have only four bonds, there are no cyclic carboxylic acids (i.e. the carboxyl group cannot form part ofa carbon ring).

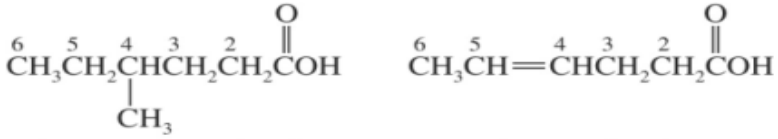


Carboxylic acids are the most polar functional group Because of the presence of hydroxyl (OH) and carbonyl (C=O) groups.

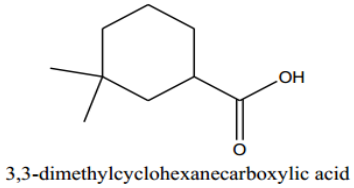


In IUPAC nomenclature, a carboxylic acid is named changing

- The **-e** of the corresponding parent alkane to **-oic** acid
- The carboxyl carbon is position ***1*** and is not numbered

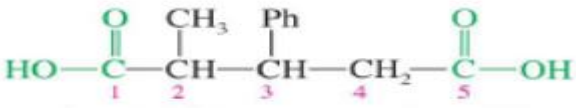


Cycloalkanes with carboxyl substituents are named as *cycloalkanes carboxylic acids.*



Aliphatic dicarboxylic acids are named by simply adding the suffix ***-dioic acid*** *to the root name.*

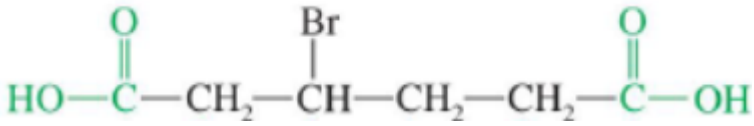
- The root name comes from the longest carbon chain containing *both carboxyl groups.*
- Numbering starts at the end closest to a substituent.



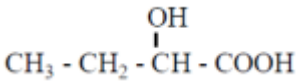
2-methyl-3-phenylpentanedioic acid

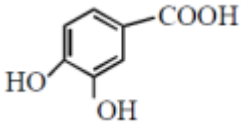
Activity

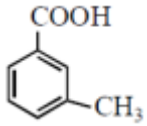
1. **What is the IUPAC Name of the following compound?**

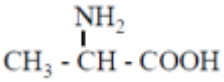
a. 

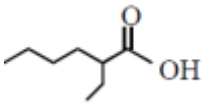
b.

c. 

e. 

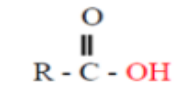
d. 

f. 

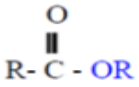
g. 

5.4. Esters compounds

Esters are derivative of carboxylic acids in which the –OH group on the carboxyl has been replaced with an –OR group.



carboxylic acid



ester

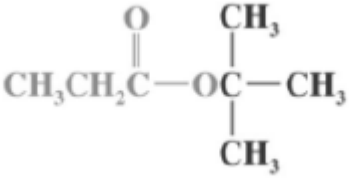
- Esters cannot form hydrogen bond to each other and therefore have lower boiling points than carboxylic acids
- Esters can hydrogen bond to water and have appreciable water Solubility

Naming of ester

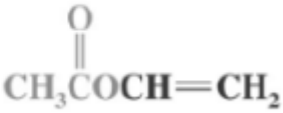
Esters are named from the corresponding carboxylic acid and alcohol from which the ester would be made

- The alcohol portion is named first and has the ending –yl
- The carboxylic acid is named ending with -ate or –oate.

Ethyl acetate



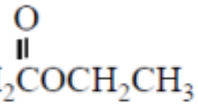
tert-butyl propanoate

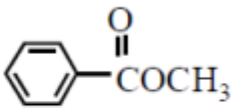


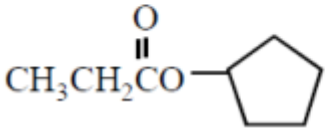
vinyl acetate (ethenylethanoate)

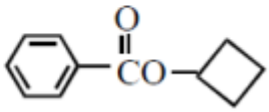
Activity

Name each of the following esters:

a) 

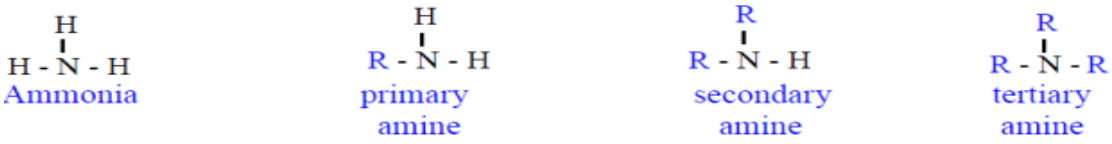
b) 

c) 

d) 

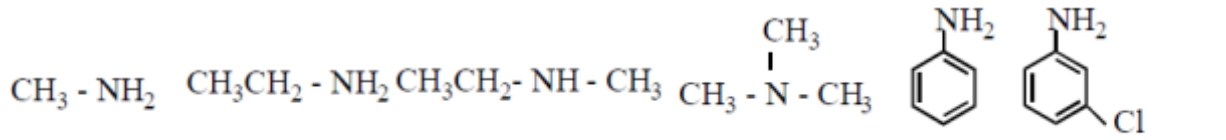
6. Amines

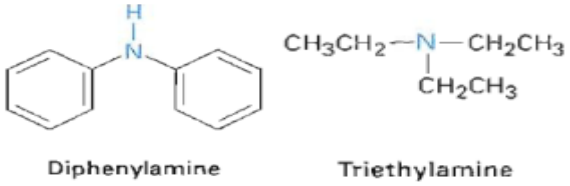
Amines are considered organic derivatives of ammonia (NH_3) in which one or more hydrogen atoms are replaced by an alkyl or aromatic group. Amines are classified as primary, secondary, or tertiary, depending on the number of organic groups directly attached to the nitrogen atom.



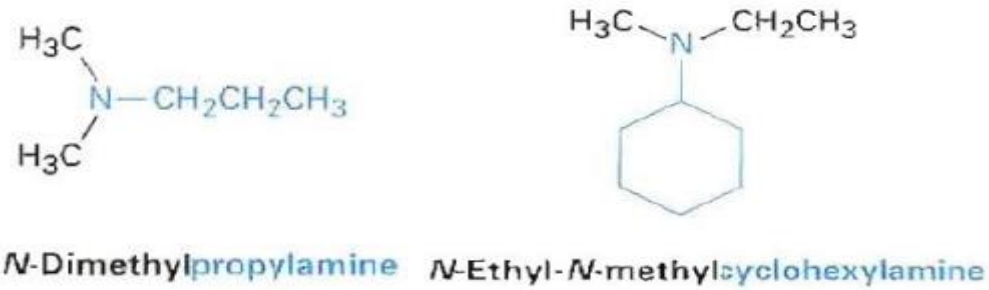
Naming of amine

- Common names are often used to name simple amines.
- If two or three alkyl groups are present, they are listed alphabetically along with the suffix –amine.
- Symmetrical secondary and teritiary amines are named by adding the prefixes di- tri- etc
- Aromatic amines are usually named based on aniline.





- Unsymmetrical substituted secondary and tertiary amines are named a *N*- substituted primary amines
- The largest alkyl group is chosen as the parent name and the other alkyl groups are side chins.



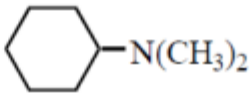
Example

Name each of the following amines:

a) $CH_3CH_2CH_2CH_2CH_2 - NH_2$

b) $CH_3CH_2CH_2CH_2 - NH\text{-}CH_2CH_2CH_2CH_3$

c) $CH_3CH_2CH_2\text{-}N(CH_3)\text{-}CH_3$ (with CH_3CHCH_3 on N)

d) 

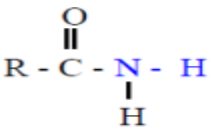
Answer

a) Pentylamineb) Dibutylamine

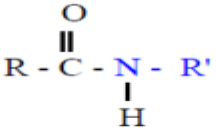
c) N-Isopropyl-N-methylpropylamined) N,N-dimethylCyclohexylamine

7. Amide

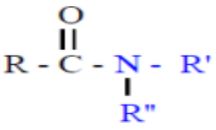
The functional group of an **amide is a carbonyl group (C = O) linked to a nitrogen atom** (N). Amides are classified as primary, secondary, and tertiary amides.



primary



secondary

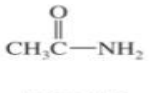


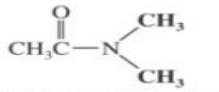
tertiary

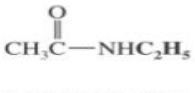
R, R′, and R″ could be aliphatic or aromatic.

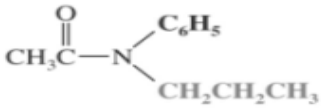
Naming of amides

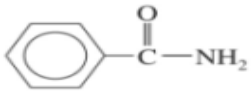
- Amides are named by replacing ***-oic acid*** *in the name with* ***amide***
- Groups on the nitrogen are named as substituents and are given the locants***N***- *or* ***N,N***-
- Amides with one or two hydrogens on nitrogen form very strong hydrogen bonds and have high melting and boiling points
- *N,N-disubstituted amides cannot form hydrogen bonds to each other and* have lower melting and boiling points


Acetamide (ethanamide) mp 82°C; bp 221°C


***N,N*-Dimethylacetamide mp −20°C; bp 166°C**

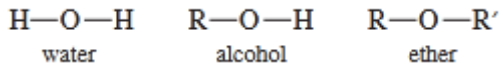

***N*-Ethylacetamide bp 205°C**


***N*-Phenyl-*N*-propylacetamide mp 49°C; bp 266°C at 712 torr**


Benzamide mp 130°C; bp 290°C

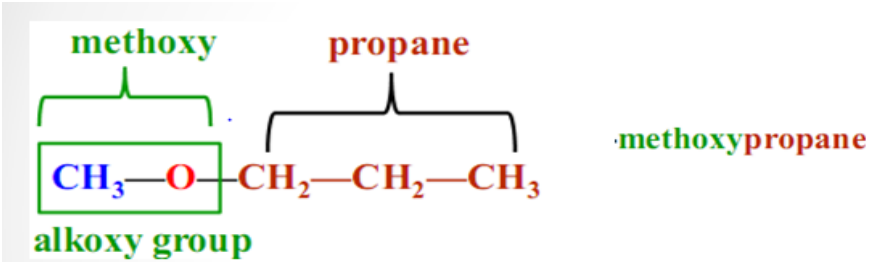
8. Ether

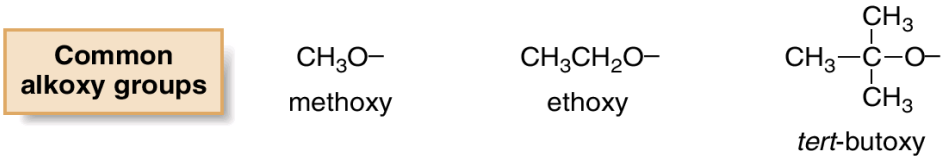
Ethers are compounds of formula R-O-R' where R and R' may be alkyl groups or aryl (benzene ring) groups. Like alcohols, ethers are related to water, with alkyl groups replacing the hydrogen atoms. In an alcohol, one hydrogen atom of water is replaced by an alkyl group. In an ether, both hydrogens are replaced by alkyl groups. The two alkyl groups are the same in a symmetrical ether and different in an unsymmetrical ether.



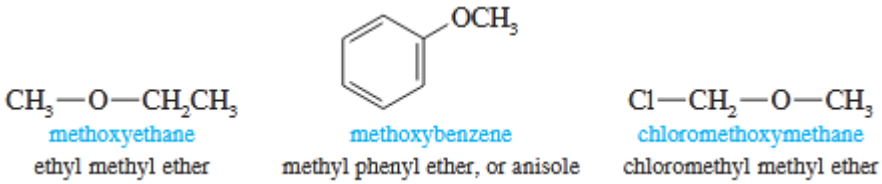
IUPAC Names (Alkoxy Alkane Names)

1. The larger of the two alkyl groups is chosen as the hydrocarbon chain.
2. The shorter alkyl group and the oxygen are named as an **alkoxy** group attached to the longer alkane.
3. Name as alkoxy name then the parent chain.



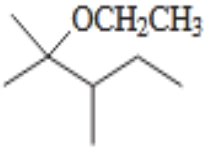


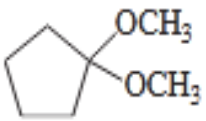
IUPAC names use the more complex alkyl group as the root name, and the rest of the ether as an alkoxy group. For example, cyclohexyl methyl ether is named methoxycyclohexane. This systematic nomenclature is often the only clear way to name complex ethers.

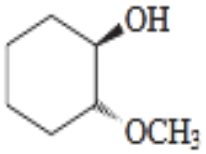


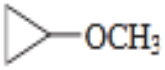
Give a systematic name for each compound.

(a) $CH_3OCH—CH_2$ (b) $CH_3CH_2OCH(CH_3)_2$ (c) $ClCH_2CH_2OCH_3$

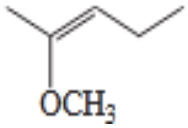
(d) 

(e) 

(f) 

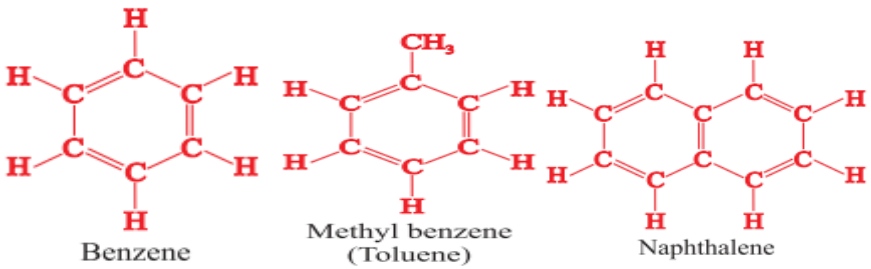
(g) 

(h) $CH_3C{\equiv}CCH_2OCH_3$

(i) 

9. Aromatic compounds

Aromatic compounds Are hydrocarbons based on the benzene ring as a structural unit. They arealso called arenes. Benzene, toluene, and naphthalene, for example, are arenes.



Historically,benzene derivatives had pleasant aromas, and were called *aromatic* compounds. But not allaromatic compounds have pleasant aromas. In the nineteenth century, many other compoundshaving properties similar to those of benzene were isolated from natural sources. Since thesecompounds possessed strong and characteristic odors, they were called aromatic compounds. Itshould be noted, however, that it is their chemical properties, and not their odor, that make themspecial.

Physical properties of arenes

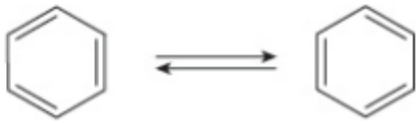
- ✓ In general, arenes resemble other hydrocarbons in their physical properties.
- ✓ They are nonpolar,
- ✓ They are insoluble in water, and less dense than water.
- ✓ In the absence of polar substituents, intermolecular forces are weak and limited to van der Waals attractions of the induced-dipole/induced-dipole type.

Any structure for benzene must account for the following facts:

- It contains a six-membered ring and three additional degrees of unsaturation.
- It is planar and should be sp2 hybridization.
- All C—C bond lengths are equal.

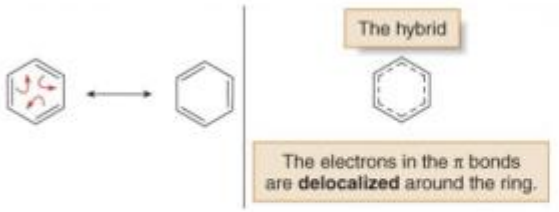
In the Kekulé description, the bond between any two carbon atoms is sometimes a single bondand sometimes a double bond.

Kekulé description: An equilibrium



The resonance description of benzene consists of two equivalent Lewis structures, each withthree double bonds that alternate with three single bonds.

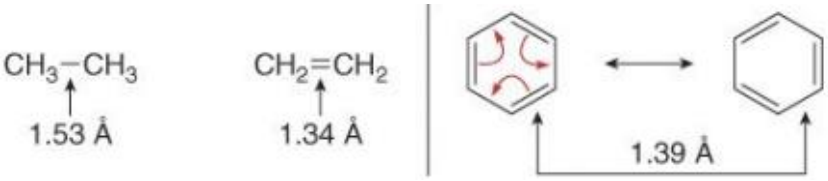
The true structure of benzene is a resonance hybrid of the two Lewis structures, with the dashedlines of the hybrid indicating the position of the π bonds.



Some texts draw benzene as a hexagon with an inner circle:

The circle represents the **six π electrons,** distributed over the six atoms of the ring.

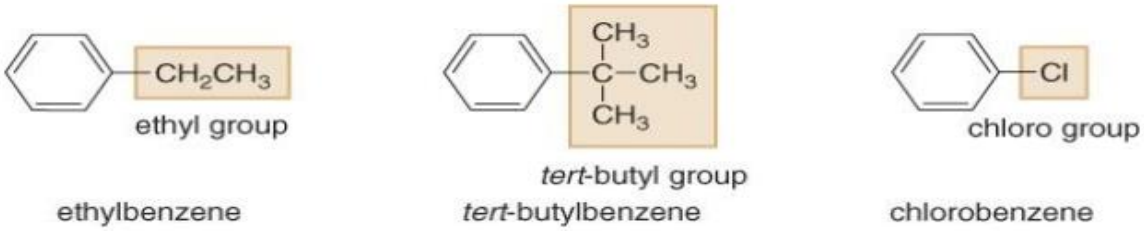
We will use one of the two Lewis structures and not the hybrid in drawing benzene. This willmake it easier to keep track of the electron pairs in the π bonds (the π electrons). In benzene, the actual bond length (1.39 Å) is intermediate between the carbon—carbon singlebond (1.53 Å) and the carbon—carbon double bond (1.34 Å).



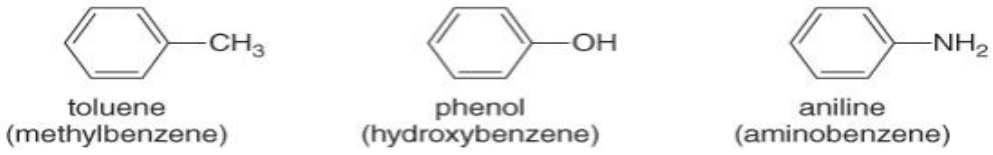
The C–C bonds in benzene are equal and intermediate in length.

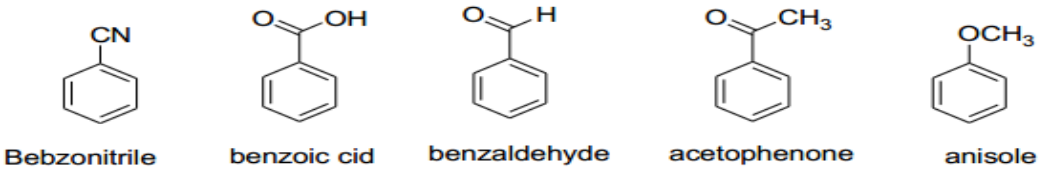
Nomenclature of Benzene Derivatives

➢ To name a benzene ring with one substituent, name the substituent and add the word benzene.

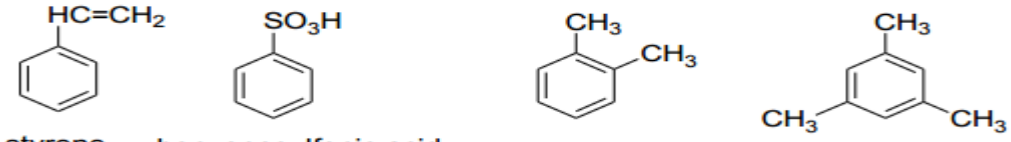


➢ Many monosubstituted benzenes have common names





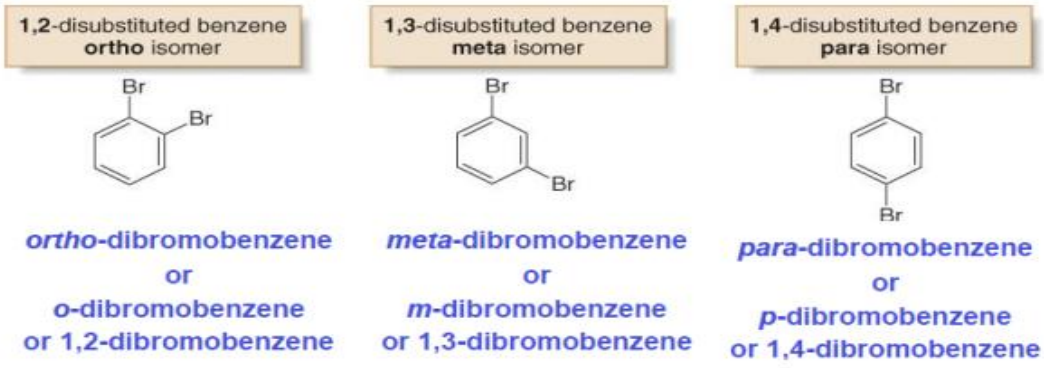
Bebzonitrile benzoic cid benzaldehyde acetophenone anisole



styrene benzonesulfonic acid o-xylene meitylene

When two substituents are present, their position may be indicated by the prefixes *ortho*, *meta*, and *para*(*o*, *m* and *p*) or by the corresponding numerical positions. They are defined as the following:

- Ortho- (o-): 1,2- substitution (next to each other in a benzene ring).
- Meta- (m): 1,3- substitution (separated by one carbon in a benzene ring).
- Para- (p): 1,4- substitution (across from each other in a benzene ring).

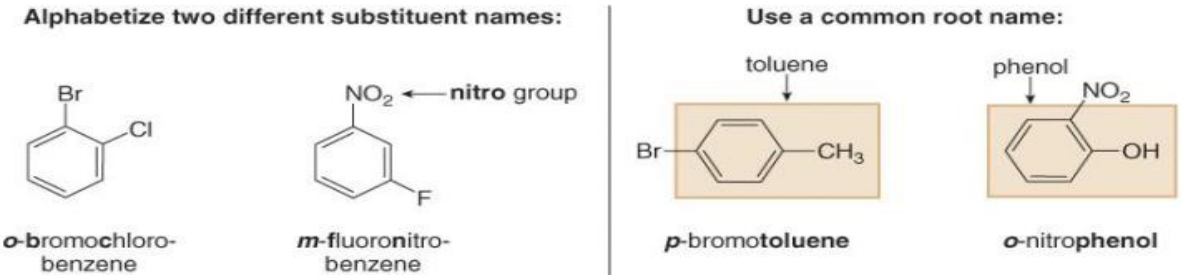


***ortho*-dibromobenzene or *o*-dibromobenzene or 1,2-dibromobenzene**

***meta*-dibromobenzene or *m*-dibromobenzene or 1,3-dibromobenzene**

***para*-dibromobenzene or *p*-dibromobenzene or 1,4-dibromobenzene**

- If the two groups on the benzene ring are different, alphabetize the names of the substituent's preceding the word benzene.
- If one substituent is part of a common root, name the molecule as a derivative of that monosubstituted benzene.



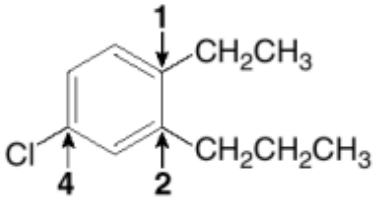
***o*-bromochloro-benzene** ***m*-fluoronitro-benzene** ***p*-bromotoluene** ***o*-nitrophenol**

- For three or more substituents on a benzene ring:
  1. Number to give the lowest possible numbers around the ring.
  2. Alphabetize the substituent names.

3. When substituents are part of common roots, name the molecule as a derivative of thatmonosubstituted benzene. The substituent that comprises the common root is located atC1.

Examples of naming polysubstituted benzenes

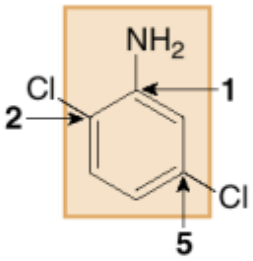
[1]



- Assign the lowest set of numbers.
- Alphabetize the names of all the substituents.

4-chloro-1-ethyl-2-propylbenzene

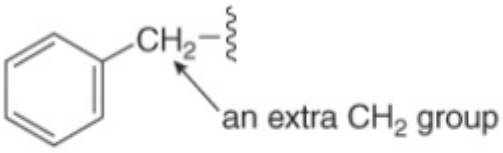
[2]



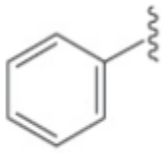
- Name the molecule as a derivative of the common root **aniline.**
- Designate the position of the NH_2 group as "1," and then assign the lowest possible set of numbers to the other substituents.

2,5-dichloroaniline

The benzyl group, another common substituent that contains a benzene ring, differs from aphenyl group.

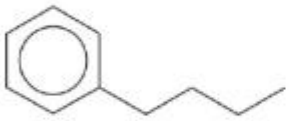


benzyl group
$C_6H_5CH_2-$

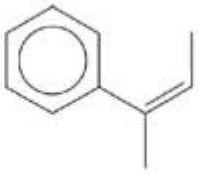


phenyl group
C_6H_5-

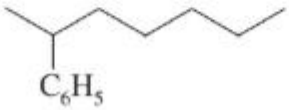
- **A hydrocarbon with a saturated chain and a benzene ring is named by choosing the larger structural unit as the parent**
- **If the chain is unsaturated then it must be the parent and the benzene is then a**



Butylbenzene

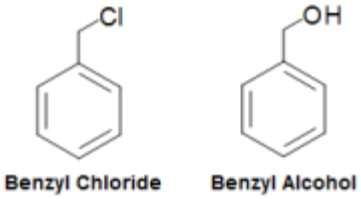


(Z)-2-Phenyl-2-butene



2-Phenylheptane

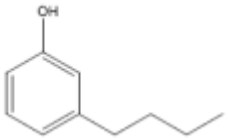
❖ Nomenclature of benzyl group based compounds is very similar to the phenyl group compounds. For example, chlorine attached to a benzyl group would simply be called benzyl chloride, whereas an OH group attached to a benzyl group would simply be called benzyl alcohol.



Benzyl Chloride Benzyl Alcohol

Activity

1. Give the IUPAC name for each compound.

a. $PhCH(CH_3)_2$ b. 

c.